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(54) Title: FORMULATED ETHYLENE/α-OLEFIN ELASTOMERIC COMPOUNDS

(57) Abstract

Formulated compositions having good uncured ("green") and cured physical properties are disclosed. The compositions comprise at least one substantially linear ethylene/$C_3$-$C_{20}$ α-olefin copolymer, or alternately, at least one linear ethylene/$C_5$-$C_{20}$ α-olefin copolymer. The compositions are easily molded and have particular utility in making wire and cable coatings.

# FORMULATED ETHYLENE/α-OLEFIN ELASTOMERIC COMPOUNDS

This application is related to pending application serial number 07/776,130, filed October 15, 1991; to copending application entitled "Elastic Substantially Linear Olefin Polymers" filed

5    September 2, 1992 in the names of Shih-Yaw Lai, George W. Knight, John R. Wilson and James C. Stevens; and to copending application entitled "Impact Modification of Thermoplastics" filed September 15, 1992 in the names of H. Craig Silvis, Daniel Murray, Thomas Fiske and Stephen R. Betso, the disclosures of each of which are incorporated

10    herein by reference.

This invention relates to compositions comprising specific ethylene/α-olefin polymers. The compositions have improved green strength, higher filler/plasticizer/oil loading capabilities and improved

15    peroxide cure efficiency.
The polymers comprise either:

       (A) at least one substantially linear ethylene/$C_3$-$C_{20}$ α-olefin polymer having specific processing characteristics, or

       (B) at least one linear ethylene/α-olefin polymer, wherein

20    the α-olefin is a $C_5$-$C_{20}$ α-olefin.

       Such compositions are useful in the automotive area, industrial goods, building and construction, electrical (for example, wire and cable coatings/insulation) and tire products.

Polymers and numerous additives are typically compounded into formulations and subsequently cross-linked for enhanced strength properties of the finished article. Additives which can be added into the formulation, depending upon the application, include oil, fillers (for

5   example, carbon black, talc, magnesium hydroxide, or calcium carbonate), co-agents (for example, triallyl cyanurate) and cross-linking agents (usually peroxide). These formulations are first compounded and mixed thoroughly to enable the various ingredients to compatibilize, since the compositions usually contain a relatively high percentage of filler. In the

10  case of a wire and cable coating operation, the compositions coat the wire and are subsequently cross-linked to stabilize the composition.

The formulated composition must have physical properties which are often mutually exclusive, depending upon the choice of the polymer. For example, the composition must have "green strength" to

15  remain on the wire after coating, and not sag or deform on the wire until the composition is cured, otherwise the wire will have thin spots and the insulating value of the composition is lost. The composition must also undergo a cure step and maintain good physical properties, such as tensile strength, elongation , and 100% modulus (stress at 100% strain).

20  Usually the polymer selected to compatibilize all of the various components is an elastomer such as ethylene/propylene rubber (EPM) or ethylene/propylene diene monomer terpolymer (EPDM). These types of very low density polymers are relatively expensive (as compared with traditional linear low density polyethylene polymers) and contain a

25  very high percentage by weight of co-monomer(s). Lowering the density of the polymer increases the ability of the polymer to hold more filler and oil. But as the polymer density decreases, the modulus of the polymer decreases, the overall composition loses uncured modulus (100% modulus) or "green strength" and performs unsatisfactorily.

30  There have been a few recent announcements regarding new polymers which are said to be effective substitutes for EPM and EPDM. Union Carbide Chemicals and Plastics Inc. announced in 1990 that they have developed a new cost effective class of polyolefins trademarked Flexomer™ Polyolefins that could replace expensive EPM or EPDM

rubbers. These new polyolefins are said to have bridged the gap between rubbers and polyethylene, having moduli between the two ranges.

In a paper presented on September 22-27, 1991 at the 1991 IEEE Power Engineering Society Transmission and Distribution Conference ("New Specialty Linear Polymers (SLP) For Power Cables," printed in the proceedings on pp. 185-190) in Dallas, Texas, Monica Hendewerk and Lawrence Spenadel, of Exxon Chemical Company, report that Exxon's Exact™ polyolefin polymers, said to be produced using single site catalyst technology, are useful in wire and cable coating applications. The new polymers are linear and said to have narrow molecular weight distruibutions, and, because of the narrow molecular weight distribution, are also said to have "the potential for melt fracture." The physical properties of filled and cross-linked formulations comprising Exact™ polymers are favorably compared with formulations comprising EP polymers in this publication. In a similar vein, in "A New Family of Linear Ethylene Polymers Provides Enhanced Sealing Performance" by Dirk G. F. Van der Sanden and Richard W. Halle, (February 1992 Tappi Journal), Exxon Chemical Company has also taught that the molecular weight distribution of a polymer is described by the polymers melt index ratio (that is, $I_{10}/I_2$) and that their new narrow molecular weight distribution polymers made using a single site catalyst are "linear backbone resins containing no functional or long chain branches."

While the development of new lower modulus polymers such as Flexomer™ Polyolefins by Union Carbide or Exact™ polymers by Exxon has aided the elastomeric formulation marketplace, there continues to be a need for other more advanced, cost-effective polymers for compounding with reasonable loadings of various fillers which improves or maintains physical properties such as "green strength" and also improves cross-linked properties such as tensile strength.

Formulated elastomeric compositions have now been discovered to have improved green strength over compositions formulated from either conventional linear ethylene/propene or ethylene/1-butene copolymers.

The compositions comprise:

a) at least one substantially linear ethylene/α-olefin copolymer, at least one curing agent, and at least one filler, wherein the α-olefin is a $C_3$-$C_{20}$ α-olefin; or

b) at least one linear ethylene/α-olefin copolymer, at least one curing agent, and at least one filler, wherein the α-olefin is a $C_5$-$C_{20}$ α-olefin.

The substantially linear ethylene/α-olefin polymers are not "linear" polymers in the traditional sense of the term, as used to describe linear low density polyethylene, nor are they highly branched polymers, as used to describe low density polyethylene. Surprisingly, however, the substantially linear olefin polymers have the process ability similar to highly branched low density polyethylene, but the strength in toughness of linear low density polyethylene.

The substantially linear ethylene/α-olefin copolymers process are characterized as having:

a) a melt flow ratio, $I_{10}/I_2, \geq 5.63$,

b) a molecular weight distribution, $M_w/M_n$, defined by the equation: $M_w/M_n \leq (I_{10}/I_2) - 4.63$, and

c) a critical shear rate at onset of surface melt fracture of at least 50 percent greater than the critical shear rate at the onset of surface melt fracture of a linear olefin copolymer having about the same $I_2$ and $M_w/M_n$.

The substantially linear ethylene/α-olefin copolymers can also be characterized as having:

a) a melt flow ratio, $I_{10}/I_2, \geq 5.63$,

b) a molecular weight distribution, $M_w/M_n$, defined by the equation: $M_w/M_n \leq (I_{10}/I_2) - 4.63$, and

c) a processing index (PI) less than or equal to about 70% of the PI of a linear olefin copolymer having about the same $I_2$ and $M_w/M_n$.

Alternately, the compositions described herein comprise linear ethylene/α-olefin copolymers, wherein the α-olefin is an α-olefin higher than $C_4$ (that is, 1-butene). Higher α-olefins (for example, $C_5$-$C_{20}$), when copolymerized with ethylene such that the polymers have

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the properties decribed herein, have been discovered to impart better physical properties to the formulated compositions than do the lower $\alpha$-olefins ($C_4$ and $C_3$).

In another aspect, the invention is a process of improving the physical properties of a cured formulated elastomeric composition, comprising the steps of:

(A) blending at least one substantially linear ethylene/$C_3$-$C_{20}$ $\alpha$-olefin copolymer, or alternately, at least one linear ethylene/$C_5$-$C_{20}$ $\alpha$-olefin copolymer, with at least one curing agent and at least one filler to form an uncured composition,

(B) forming a structure with the uncured composition of (A), and

(C) curing the structure of (B).

The formulated compositions described herein have good green strength and maintain adequate modulus, relative to conventional linear ethylene/propene copolymers or linear ethylene/1-butene copolymers when incorporated at about the same levels.

The term "substantially linear" ethylene/$\alpha$-olefin polymers means that the polymer backbone is substituted with 0.01 long chain branches/1000 carbons to 3 long chain branches/1000 carbons, more preferably from 0.01 long chain branches/1000 carbons to 1 long chain branches/1000 carbons, and especially from 0.05 long chain branches/1000 carbons to 1 long chain branches/1000 carbons.

The substantially linear ethylene/$\alpha$-olefin polymers and interpolymers of the present invention are herein defined as in copending application serial number 07/776,130 and in copending application entitled "Elastic Substantially Linear Olefin Polymers" filed September 2, 1992 in the names of Shih-Yaw Lai, George W. Knight, John R. Wilson and James C. Stevens. The substantially linear ethylene/$\alpha$-olefin polymers and interpolymers useful for forming the compositions described herein are those in which the comonomer is randomly distributed within a given interpolymer molecule and

wherein substantially all of the interpolymer molecules have the same ethylene/comonomer ratio within that interpolymer.

Long chain branching is defined herein as a chain length of at least about 6 carbons, above which the length cannot be distinguished
5  using $^{13}C$ nuclear magnetic resonance spectroscopy. The long chain branch can be as long as about the same length as the length of the polymer back-bone.

Long chain branching is determined by using $^{13}C$ nuclear magnetic resonance (NMR) spectroscopy and is quantified using the
10  method of Randall (Rev. Macromol.Chem. Phys., C29 (2&3), p. 285-297), the disclosure of which is incorporated herein by reference.

The substantially linear ethylene/α-olefin polymers or copolymers for use in the present invention are interpolymers of ethylene with at least one $C_3$-$C_{20}$ α-olefin and/or $C_4$-$C_{18}$ diolefins. Interpolymers of
15  ethylene and 1-octene are especially preferred. The term "interpolymer" is used herein to indicate a copolymer, or a terpolymer, or the like. That is, at least one other comonomer is polymerized with ethylene to make the interpolymer.

Other unsaturated monomers usefully copolymerized with
20  ethylene include, for example, ethylenically unsaturated monomers, conjugated or nonconjugated dienes, polyenes, etc. Preferred comonomers include the $C_3$-$C_{20}$ α-olefins especially propene, isobutylene, 1-butene, 1-hexene, 4-methyl-1-pentene, and 1-octene. Other preferred monomers include styrene, halo- or alkyl substituted styrenes, tetrafluoroethylene,
25  vinylbenzocyclobutane, 1,4-hexadiene, and naphthenics (for example, cyclopentene, cyclohexene and cyclooctene).

The term "linear ethylene/α-olefin copolymers" means that the olefin copolymer does not have long chain branching. That is, the linear ethylene/α-olefin copolymer has an absence of long chain branching,
30  as for example the linear low density polyethylene polymers or linear high density polyethylene polymers made using uniform branching distribution polymerization processes (for example, USP 3,645,992 (Elston), the disclosure of which is incorporated herein by reference) and are those in which the comonomer is randomly distributed within a given interpolymer

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molecule and wherein substantially all of the interpolymer molecules have the same ethylene/comonomer ratio within that interpolymer. The term "linear ethylene/$\alpha$-olefin polymers" does not refer to high pressure branched (free-radical polymerized) polyethylene which is known to those

5    skilled in the art to have numerous long chain branches. The linear ethylene/$\alpha$-olefin polymers are ethylene/$\alpha$-olefin interpolymers having a short chain branching distribution index (SCBDI) greater than about 30 percent. The $\alpha$-olefin is at least one $C_5$-$C_{20}$ $\alpha$-olefin (for example, 1-pentene, 4-methyl-1-pentene, 1-hexene, 1-octene), preferably wherein at

10   least one of the $\alpha$-olefins is 1-octene. The linear ethylene/$\alpha$-olefin polymers have a single melting point, as opposed to traditional Ziegler polymerized polymers having two or more melting points, as determined using differential scanning calorimetry (DSC).

The density of the linear or the substantially linear olefin
15   polymers or copolymers (as measured in accordance with ASTM D-792) for use in the present invention is generally less than 0.94 g/cm$^3$, preferably from 0.85 g/cm$^3$ to 0.9 g/cm$^3$, and especially from 0.86 g/cm$^3$ to 0.89 g/cm$^3$. The density of the linear or the substantially linear olefin polymers or copolymers used in the present invention is generally

20   dependent upon the amount and the type of oil compounded into the formulation. Generally, the higher the oil content, the lower the density of the copolymer used in the formulation.

Additionally, the density of the linear or substantially linear ethylene/$\alpha$-olefin polymer has been discovered to influence or control the

25   cure properties of the final composition. The higher the density of the linear or substantially linear ethylene/$\alpha$-olefin polymer, the higher the rate of cure of the formulated composition (that is, delta torque divided by delta time) measured by increased torque using an Oscillating Disk Rheometry (ODR)) and the higher the extent or degree of cure (as determined by

30   testing the final torque or molecular weight of the cross-linked matrix/composition), holding the polymer molecular weight, and level of peroxide used about constant.

Generally, the amount of the linear or the substantially linear olefin polymer incorporated into the composition is from 10 percent to 95

percent, by weight of the composition, preferably 20 percent to 80 percent, by weight of the composition, and especially from 25 percent to 65 percent, by weight of the composition.

The molecular weight of the linear or the substantially linear
5   olefin polymers for use in the present invention is conveniently indicated using a melt index measurement according to ASTM D-1238, Condition 190 °C/2.16 kg (formerly known as "Condition (E)" and also known as $I_2$). Melt index is inversely proportional to the molecular weight of the polymer. Thus, the higher the molecular weight, the lower the melt index, although
10  the relationship is not linear. The melt index for the substantially linear olefin polymers useful herein is generally from 0.01 grams/10 minutes (g/10 min) to 30 g/10 min, preferably from 0.05 g/10 min to 10 g/10 min, and especially from 0.1 g/10 min to 5 g/10 min.

Another measurement useful in characterizing the molecular
15  weight of the substantially linear olefin polymers is conveniently indicated using a melt index measurement according to ASTM D-1238, Condition 190 °C/10 kg (formerly known as "Condition (N)" and also known as $I_{10}$). The ratio of these two melt index terms is the melt flow ratio and is designated as $I_{10}/I_2$. Generally, the $I_{10}/I_2$ ratio for the linear is at least 5.63, preferably
20  at least 7, especially at least 8 or above. For the substantially linear ethylene/α-olefin polymers used in the compositions of the invention, the $I_{10}/I_2$ ratio indicates the degree of long chain branching, that is, the higher the $I_{10}/I_2$ ratio, the more long chain branching in the polymer. Generally, the $I_{10}/I_2$ ratio of the substantially linear ethylene/α-olefin polymers is at
25  least about 5.63, preferably at least about 7, especially at least about 8 or above.

Other additives such as antioxidants (for example, hindered phenolics (for example, Irganox® 1010 made by Ciba Geigy Corp.), phosphites (for example, Irgafos® 168)), cling additives (for example, PIB),
30  antiblock additives, pigments, fillers, coupling agents (for example, vinyl-tris(2 methoxyethoxy)- silane (A-172 made by Union Carbide) can also be included in the formulations, to the extent that they do not interfere with the enhanced formulation properties discovered by Applicants.

The "rheological processing index" (PI) is the apparent viscosity (in kpoise) of a polymer measured by a gas extrusion rheometer (GER). The gas extrusion rheometer is described by M. Shida, R.N. Shroff and L.V. Cancio in Polymer Engineering Science, Vol. 17, no. 11, p. 770

5   (1977), and in "Rheometers for Molten Plastics" by John Dealy, published by Van Nostrand Reinhold Co. (1982) on page 97-99, both publications of which are incorporated by reference herein in their entirety. All GER experiments are performed at a temperature of 190°C, at nitrogen pressures between 5250 to 500 psig using a 0.0296 inch diameter, 20:1 L/D die with

10  an entrance angle of 180°. For the polymers described herein, the PI is the apparent viscosity (in kpoise) of a material measured by GER at an apparent shear stress of $2.15 \times 10^6$ dyne/$cm^2$. The novel polymers described herein preferably have a PI in the range of 0.01 kpoise to 50 kpoise, preferably about 15 kpoise or less. The novel substantially linear

15  olefin polymers described herein for use ion the compositions have a PI less than or equal to about 70% of the PI of a comparative linear olefin polymer at about the same $I_2$ and $M_w/M_n$.

An apparent shear stress vs. apparent shear rate plot is used to identify the melt fracture phenomena. According to Ramamurthy in

20  Journal of Rheology, 30(2), 337-357, 1986, above a certain critical flow rate, the observed extrudate irregularities may be broadly classified into two main types: surface melt fracture and gross melt fracture.

Surface melt fracture occurs under apparently steady flow conditions and ranges in detail from loss of specular gloss to

25  the more severe form of "sharkskin". In this disclosure, the onset of surface melt fracture (OSMF) is characterized at the beginning of losing extrudate gloss at which the surface roughness of extrudate can only be detected by 40X magnification. The critical shear rate at onset of surface melt fracture for the substantially linear olefin polymers is at least 50 percent greater

30  than the critical shear rate at the onset of surface melt fracture of a linear olefin polymer having about the same $I_2$ and $M_w/M_n$.
Gross melt fracture occurs at unsteady flow conditions and ranges in detail from regular (alternating rough and smooth, helical, etc.) to random distortions. The critical shear rate at onset of surface melt fracture (OSMF)

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and onset of gross melt fracture (OGMF) will be used herein based on the changes of surface roughness and configurations of the extrudates extruded by a GER.

5    The SCBDI (Short Chain Branch Distribution Index) or CDBI (Composition Distribution Branch Index) is defined as the weight percent of the polymer molecules having a comonomer content within 50 percent of the median total molar comonomer content. The CDBI of a polymer is readily calculated from data obtained from techniques known in the art, such as, for example, temperature rising elution fractionation (abbreviated

10   herein as "TREF") as described, for example, in Wild et al, Journal of Polymer Science, Poly. Phys. Ed., Vol. 20, p. 441 (1982), or in U.S. Patent 4,798,081, both disclosures of which are incorporated herein by reference. The SCBDI or CDBI for the linear and for the substantially linear olefin polymers of the present invention is preferably greater than about 30

15   percent, especially greater than about 50 percent.

## Molecular Weight Distribution Determination of the Linear or Substantially Linear Olefin Polymers

The linear or substantially linear olefin interpolymer product

20   samples are analyzed by gel permeation chromatography (GPC) on a Waters 150C high temperature chromatographic unit equipped with three mixed porosity columns (Polymer Laboratories $10^3$, $10^4$, $10^5$, and $10^6$), operating at a system temperature of 140°C. The solvent is 1,2,4-trichlorobenzene, from which 0.3 percent by weight solutions of the

25   samples are prepared for injection. The flow rate is 1.0 milliliters/minute and the injection size is 200 microliters.

The molecular weight determination is deduced by using narrow molecular weight distribution polystyrene standards (from Polymer Laboratories) in conjunction with their elution volumes. The

30   equivalent polyethylene molecular weights are determined by using appropriate Mark-Houwink coefficients for polyethylene and polystyrene (as described by Williams and Word in Journal of Polymer Science, Polymer Letters, Vol. 6, (621) 1968, incorporated herein by reference) to derive the following equation:

$$M_{polyethylene} = a * (M_{polystyrene})^b.$$

In this equation, $a = 0.4316$ and $b = 1.0$. Weight average molecular weight,
$M_w$, is calculated in the usual manner according to the following formula:
$M_w = R\ w_i * M_i$, where $w_i$ and $M_i$ are the weight fraction and molecular
weight, respectively, of the $i^{th}$ fraction eluting from the GPC column.

For both the linear and the substantially linear ethylene/α-
olefin polymers, the $M_w/M_n$ is preferably from 1.5 to 2.5, especially about
2.


The Substantially Linear Olefin Polymers

The substantially linear ethylene/α-olefin polymers are made
by using suitable constrained geometry catalysts, preferably constrained
geometry catalysts as disclosed in U.S. Application Serial Nos.: 545,403,
filed July 3, 1990; 758,654, filed September 12, 1991; 758,660, filed
September 12, 1991; and 720,041, filed June 24, 1991, the teachings of all of
which are incorporated herein by reference. The monocyclopentadienyl
transition metal olefin polymerization catalysts taught in USP 5,026,798, the
teachings of which is incorporated herein by reference, are also suitable for
use in preparing the polymers of the present invention, so long as the
reaction conditions are as specified below.

Suitable cocatalysts for use herein include but are not limited
to, for example, polymeric or oligomeric aluminoxanes, especially methyl
aluminoxane, as well as inert, compatible, noncoordinating, ion forming
compounds. Preferred cocatalysts are inert, noncoordinating, boron
compounds.


Polymerization of the Substantially Linear Ethylene/α-Olefin Polymer

The polymerization conditions for manufacturing the
substantially linear ethylene/α-olefin polymers of the present invention are
generally those useful in the solution polymerization process, although the
application of the present invention is not limited thereto. Slurry and gas

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phase polymerization processes are also believed to be useful, provided the proper catalysts and polymerization conditions are employed.

Multiple reactor polymerization processes can also be used in making the substantially linear olefin polymers and copolymers of the

5    present invention, such as those disclosed in USP 3,914,342, incorporated herein by reference. The multiple reactors can be operated in series or in parallel, with at least one constrained geometry catalyst employed in one of the reactors.

10    The Formulated Compositions

The compositions disclosed herein generally comprise: the copolymer in amounts of about 10-95 % (by total formulation weight) ; at least one (active (that is, imparting a particular property, for example, ignition resistance) or inactive (that is, used primarily as a cost reducer))

15    filler (for example, carbon black or mineral fillers (for example, aluminum trihydrate (ATH), calcium carbonate, or silicon treated clay (for example, Whitex clay made by Freeport Kaolin))); an optional process oil(s) (for example, paraffinic oil (for example, Sunpar™ 2280 made by Sun Oil Company); an optional process aid(s) (for example, paraffin wax, stearic

20    acid); at least one curing agent (for example, a peroxide (for example, VULCUP™ 40 KE (a,a'-bis(t-butylperoxy)-diisopropylbenzene made by Hercules, Inc.), Di-cup™ (a series of vulcanizing and polymerization agents containing dicumyl peroxide made by Hercules, Inc.), Lupersol™ (1,1,-bis-t-butylperoxy)-3,3,5 trimethylcyclohexane made by Atochem, North

25    America) or Trigonox™ (an organic peroxide made by Noury Chemical Corporation)); other curing agents, for example, radiation curing (β), can also be used to cure the compositions disclosed herein); and an optional coagent (for example, triallyl cyanurate (TAC), made by American Cyanamide; SR-350, a trimethylpropane trimethacrylate made by Sartomer

30    Resins, Inc.).

Lower peroxide levels can also be used in the compositions disclosed herein without loss of physical properties, which is especially beneficial since the peroxide is usually the highest cost component of the formulation.

The formulations are compounded by any convenient method, including dry blending the individual components and subsequently melt mixing or by pre-melt mixing in a separate extruder (for example, a Banbury mixer, a Haake mixer, a Brabender internal mixer, or a

5    twin screw extruder).

There are many types of molding operations which can be used to form useful fabricated articles or parts from the formulations disclosed herein, including various injection molding processes (for example, that described in Modern Plastics Encyclopedia/89, Mid October

10   1988 Issue, Volume 65, Number 11, pp. 264-268, "Introduction to Injection Molding" and on pp. 270-271, "Injection Molding Thermoplastics", the disclosures of which are incorporated herein by reference) and blow molding processes (for example, that described in Modern Plastics Encyclopedia/89, Mid October 1988 Issue, Volume 65, Number 11, pp. 217-

15   218, "Extrusion-Blow Molding", the disclosure of which is incorporated herein by reference), profile extrusion, calandering, pultrusion. Some of the fabricated articles include automotive hoses, single ply roofing, and wire and cable voltage insulation and jackets.

20   Experimental

For each of the examples (unless otherwise specified) and the comparative examples, a blend containing 100 parts (by weight of the total composition) of the selected polymer, 100 parts of a filler (carbon black N550), 50 parts of a process oil (Sunpar™ 2280), 5 parts of a paraffin wax

25   process aid, 1 part of a stearic acid process aid, 8 parts of a peroxide (VULCUP 40KE, 40% peroxide on a Burgess KE clay sold by Hercules, Inc.) and 1.5 parts of a coagent (triallyl cyanurate, TAC) are compounded on a Haake mixer, a Banbury mixer, or a Brabender internal mixer. The mixer was selected according to the expected sample size. For each sample, the

30   mixing bowl was preheated to about 80°C. A premix was made comprising filler and process oil and aids. The premix was added to the internal mixer first (upside down mix) and the selected polymer was then added and allowed to masticate. The cure package was then added (note: the cure package can be added with the premix). The entire mixture was

mixed until a bowl temperature of 110°C was reached, when the compound
was then dropped from the mixer. The formulation was optionally passed
through a roll mill until the formulation was consistent in appearance.

The formulations are tested both in the uncured state and in
5    the cured state. The uncured formulations are formed into plaques by
compression molding at 260°F for 5 minutes. The formuations are cured by
placing the compression molded blankets into a mold and compression
mold cured at 350°F for 24 minutes.

The tests performed on the various formulations include:
10   ODR (which provides a measure of cure in the elastomeric compound, per
ASTM D-2084-75, incorporated herein by reference); stress-strain of cured
and uncured compounds; and other physical properties of the cured
compound. Mooney viscosity, measured using a shear rheometer which
obtains a minimum Mooney torque viscosity and may be used to obtain
15   scorch and compound cure characteristics, (per ASTM D 1646-89,
incorporated herein by reference) was run on the uncured samples and
other tests are also performed if the sample size allows.

Examples 1-3
20   Examples 1-3 use an ethylene/1-octene copolymer produced using the
constrained geometry catalyst technology described earlier, using a
continuous process, having $I_2$ of about 0.63 g/10 minutes and a density of
about 0.8697 g/cm$^3$. The neat (that is, uncompounded and uncured)
polymer, as well as the compounded formulation and cured (using 100% of

the peroxide (that is, 8 parts)) formulation physical properties were shown
in Table 1:

Table 1

|  | Neat | Compounded ("Green") | Cured |
|---|---|---|---|
| Tensile Strength (psi) | 1581 | 1629 | 2053 |
| 100% Modulus* | 334 | 467 | 996 |
| Elongation at break (%) | 821 | 915 | 252 |

*Stress at 100% strain

5

Examples 2 and 3 were also run using 90% of the peroxide and 80% of the
formulated peroxide, with the polymer described for Example 1. The
physical properties of the compounded formulations and the cured
formulations was shown in Table 2:

10

Table 2

|  | Example 2 Compounded ("Green") (90% peroxide) | Example 3 Compounded ("Green") (80% peroxide) | Ex. 2 Cured (90% peroxide) | Ex. 3 Cured (80% peroxide) |
|---|---|---|---|---|
| Tensile Strength (psi) | 1579 | 1544 | 2110 | 2123 |
| 100% Modulus* | 465 | 479 | 931 | 900 |
| Elongation at break (%) | 853 | 832 | 312 | 325 |

*Stress at 100% strain

15   Comparing the physical properties for both the compounded "green"
formulations of the 100% peroxide cured compositions of Example 1 with

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the properties of the 90% and 80% peroxide cured compositions of
Examples 2 and 3, lower quantities of the peroxide can be used in the novel
formulations of the invention and still maintain adequate physical
properties of the composition, both in the uncured ("green") formulations
5   and in the cured formulations.


Example 4 and Comparative Example 5

Example 4 incorporates a substantially linear ethylene/1-
octene copolymer produced using the constrained geometry catalyst
10   technology described earlier in a continuous polymerization process having
$I_2$ of about 0.5 g/10 minutes and a density of about 0.8695 g/cm$^3$.

Comparative Example 5 incorporates Vistalon™ 707, an
ethylene/propene elastomer having a density of about 0.87 g/cm$^3$ and $I_2$ of
about 0.4 g/10 minutes sold by Exxon Chemical.
15   Physical properties of the resultant uncured and cured
compositions was shown in Table 3:

Table 3

| | Example 4 Compounded ("Green") | Comparative Example 5 Compounded ("Green") | Ex. 4 Cured | Comp. Ex. 5 Cured |
|---|---|---|---|---|
| Tensile Strength (psi) | 1637 | 459 | 2223 | 1569 |
| 100% Modulus* | 429 | 231 | 937 | 609 |
| Elongation at break (%) | 870 | 685 | 302 | 310 |

As the data indicate, the composition of the invention has
better uncured and cured properties, especially tensile strength and
modulus, than a composition made using a commercial ethylene/propene
elastomer having about the same melt index and density.


Example 6 and Comparative Example 7

Example 6 incorporates a substantially linear ethylene/1-
octene copolymer produced using the constrained geometry catalyst
technology described earlier in a continuous polymerization process having
$I_2$ of about 0.63 g/10 minutes, $M_w/M_n$ of about 2, $I_{10}/I_2$ of about 7.8, and a
density of about 0.8697 g/cm$^3$.

Comparative Example 7 incorporates Tafmer™ P-0680, a
linear ethylene/propene elastomer having a density of about 0.867 g/cm$^3$,
$I_2$ of about 0.4 g/10 minutes, $M_w/M_n$ of about 2, and $I_{10}/I_2$ of about 6.23,
sold by Mitsui PetroChemical.

Physical properties of the resultant uncured and cured
compositions was shown in Table 4:

Table 4

| | Example 6 Compounded ("Green") | Comparative Example 7 Compounded ("Green") | Ex. 6 Cured | Comp. Ex. 7 Cured |
|---|---|---|---|---|
| Tensile Strength (psi) | 1629 | 356 | 2053 | 1734 |
| 100% Modulus* | 467 | 231 | 996 | 496 |
| Elongation at break (%) | 915 | 490 | 252 | 301 |

As the data indicate, the composition of the invention has better uncured and cured properties, especially tensile strength and modulus, than a composition made using a linear ethylene/propene copolymer having about the same melt index, density and $M_w/M_n$, but differing melt flow ratio ($I_{10}/I_2$).

## Example 8 and Comparative Example 9

Example 8 incorporates an ethylene/propene copolymer produced using the constrained geometry catalyst technology described earlier in a continuous polymerization process, and has an $I_2$ of about 1 g/10 minutes and a density of about 0.87 g/cm$^3$.

Comparative Example 9 incorporates Vistalon™ 7000, an ethylene/propene/diene elastomer having a density of about 0.875 g/cm$^3$ and $I_2$ of about 0.06 g/10 minutes sold by Exxon Chemical. Note that the molecular weight (as indicated by lower $I_2$) of the Vistalon™ 7000 was considerably higher than that of the ethylene/propene copolymer used in Example 8, but that the physical properties of the formulated compositions of Example 8 were at least as good as or better than those of the formulated compositions of Comparative Example 9.

Physical properties of the resultant uncured and cured compositions was shown in Table 5:

Table 5

|  | Example 8 Compounded ("Green") | Comparative Example 9 Compounded ("Green") | Ex. 8 Cured | Comp. Ex. 9 Cured |
|---|---|---|---|---|
| Tensile Strength (psi) | 450 | 401 | 1068 | 1193 |
| 100% Modulus* | 297 | 313 | 692 | 707 |
| Elongation at break (%) | 993 | 458 | 259 | 251 |

### Examples 10-12

Example 10 incorporates a substantially linear ethylene/1-octene copolymer produced using the constrained geometry catalyst technology described earlier in a continuous polymerization process having $I_2$ of about 0.99 g/10 minutes, $M_w/M_n$ of about 1.917, $I_{10}/I_2$ of about 7.5, and a density of about 0.871 g/cm$^3$.

Example 11 incorporates a substantially linear ethylene/1-octene copolymer produced using the constrained geometry catalyst technology described earlier in a continuous polymerization process having $I_2$ of about 0.88 g/10 minutes, $M_w/M_n$ of about 2.016, $I_{10}/I_2$ of about 8.0, and a density of about 0.88 g/cm$^3$.

Example 12 incorporates a substantially linear ethylene/1-octene copolymer produced using the constrained geometry catalyst technology described earlier in a continuous polymerization process having $I_2$ of about 0.83 g/10 minutes, $M_w/M_n$ of about 2.201, $I_{10}/I_2$ of about 8.5, and a density of about 0.902 g/cm$^3$.

For Examples 10-12, the composition comprised 100 parts of the selected polymer, 130 parts of ATH (alumina trihydrate, a mineral filler

used to reduce the formulation cost and as a flame retardant), 7.5 parts of VULKUP 40KE (40% peroxide on a Burgess KE clay used as a curing agent) and 1.2 parts of TAC ( triallyl cyanurate, an organic coagent used to enhance the cure rate/state). Table 6 shows the minimum (ML) and
5    maximum (that is, plateau) torque (MH) values for the compositions as they cure and the difference between the torque values (used as the measure of the final cure state), as described in ASTM D 2084-75, for Examples 10-12. For these Examples, the time to reach 90% of the final cure state (T90) was defined using the equation:
10              $Mc_{90} = 0.9(MH - ML) + ML$.

$T_{90}$ was the time to reach $Mc_{90}$. For Examples 10-12, $T_{90}$ was about 5.9 minutes.

Table 6

|  | Ex. 10 | Ex. 11 | Ex. 12 |
|---|---|---|---|
| Minimum Torque (lb-inch) | 16 | 15 | 17 |
| Maximum Torque (lb-inch) | 165 | 182 | 190 |
| Torque Difference | 149 | 167 | 173 |
| Rate of Torque Increase (torque difference divided by $T_{90}$) (lb-in/minute) | 25.3 | 28.3 | 29.3 |

15    As the data indicate, the torque difference increases with increasing density of the polymer selected for use in the composition. Increasing the torque corresponds to improved cure properties of composition. Thus, the cure process of the composition can be controlled by varying the density of the selected polymer. The rate of torque also increases with increasing
20    polymer density.

We Claim:

1. A formulated elastomeric composition comprising at least one substantially linear ethylene/α-olefin copolymer, at least one curing agent, and at least one filler, wherein the substantially linear ethylene/α-olefin copolymer was characterized as having:

5
a) a melt flow ratio, $I_{10}/I_2 \geq 5.63$,

b) a molecular weight distribution, $M_w/M_n$, defined by the equation: $M_w/M_n \leq (I_{10}/I_2) - 4.63$, and

c) a critical shear rate at onset of surface melt fracture of at least 50 percent greater than the critical shear rate at the onset

10
of surface melt fracture of a linear ethylene/α-olefin copolymer having about the same $I_2$ and $M_w/M_n$.

2. A formulated elastomeric composition comprising at least one substantially linear ethylene/α-olefin copolymer , at least one curing

15
agent, and at least one filler, wherein the substantially linear ethylene/α-olefin copolymer was characterized as having:

a) a melt flow ratio, $I_{10}/I_2 \geq 5.63$,

b) a molecular weight distribution, $M_w/M_n$, defined by the equation: $M_w/M_n \leq (I_{10}/I_2) - 4.63$, and

20
c) a processing index less than or equal to about 70% of the PI of a linear ethylene/α-olefin copolymer having about the same $I_2$ and $M_w/M_n$.

3. A formulated elastomeric composition comprising at least

25
one substantially linear ethylene/α-olefin copolymer, at least one curing

agent, and at least one filler, wherein the substantially linear ethylene/α-olefin copolymer was characterized as having:

a) a melt flow ratio, $I_{10}/I_2, \geq 5.63$, and

b) a molecular weight distribution, $M_w/M_n$, from 1.5 to 2.5.

5

4. The composition of Claims 1, 2, or 3 wherein the $I_{10}/I_2$ of the substantially linear ethylene/α-olefin copolymer is at least about 7.

5. The composition of Claims 1, 2, or 3 wherein the $I_{10}/I_2$ of

10      the substantially linear ethylene/α-olefin copolymer is at least about 8.

6. The composition of Claims 1, 2, or 3 wherein the substantially linear ethylene/α-olefin copolymer is a copolymer of ethylene and at least one $C_3$-$C_{20}$ α-olefin.

15

7. The composition of Claims 1, 2, or 3 wherein the substantially linear ethylene/α-olefin copolymer is a copolymer of ethylene and at least one $C_4$-$C_{20}$ α-olefin.

20      8. The composition of Claims 1, 2, or 3 wherein the substantially linear ethylene/α-olefin copolymer is a copolymer of ethylene and at least one $C_8$-$C_{20}$ α-olefin.

9. The composition of Claims 1, 2, or 3 wherein the

25   substantially linear ethylene/α-olefin copolymer is a copolymer of ethylene and 1-octene.

10. The composition of Claims 1, 2, or 3 wherein the substantially linear ethylene/α-olefin copolymer has from 0.01 to 3 long

30   chain branches/1000 carbons along the polymer backbone.

11. A fabricated article made from the composition of Claims 1, 2, or 3.

12. A process of improving the physical properties of a cured formulated elastomeric composition, comprising the steps of:

(A) blending at least one substantially linear ethylene/$C_3$-$C_{20}$ α-olefin copolymer with at least one curing agent and at least one filler to

5     form an uncured composition,

(B) forming a structure with the uncured composition of (A), and

(C) curing the structure of (B).

10     13. The process of Claim 12 wherein the curing agent of (A) comprises a peroxide curing agent.

14. The process of Claim 12 further comprising the step of increasing the rate of cure of the formulated composition by selecting the

15     substantially linear ethylene/α-olefin copolymer to have a density from 0.85 g/$cm^3$ to 0.92 g/$cm^3$.

15. A process of improving the physical properties of a cured formulated elastomeric composition, comprising the steps of:

20     (A) blending at least one linear ethylene/$C_5$-$C_{20}$ α-olefin copolymer with at least one curing agent and at least one filler to form an uncured composition,

(B) forming a structure with the uncured composition of (A), and

25     (C) curing the structure of (B).

16. The process of Claim 15 wherein the curing agent of (A) comprises a peroxide curing agent.

30     17. The process of Claim 16 further comprising the step of increasing the rate of cure of the formulated composition by selecting the substantially linear ethylene/α-olefin copolymer to have a density from 0.85 g/$cm^3$ to 0.92 g/$cm^3$.

18.  A formulated elastomeric composition comprising at least one linear ethylene/α-olefin copolymer, at least one curing agent, and at least one filler, wherein the α-olefin is a $C_5$-$C_{20}$ α-olefin.

5          19. The composition of Claim 18 wherein at least one of the α-olefins is 1-octene.

20.  A fabricated article made from the composition of Claim 18.

10

# INTERNATIONAL SEARCH REPORT

**A. CLASSIFICATION OF SUBJECT MATTER**

IPC 5    C08L23/04    C08L23/16

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

IPC 5    C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| P,X | WO,A,93 04486 (EXXON CHEMICAL PATENTS INC.) 4 March 1993 see page 10, line 34 - page 18, line 12; claims 1-11 | 1-11 |
| A | DATABASE WPI Section Ch, Week 8841, Derwent Publications Ltd., London, GB; Class A85, AN 88-288752 & JP,A,63 210 150 (DAINICHI NIPPON CABLES) 31 August 1988 see abstract | 1-20 |

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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| Date of the actual completion of the international search | Date of mailing of the international search report |
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| 11 January 1994 | 2 1. 01. 94 |

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| European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016 | Clemente Garcia, R |

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|---|---|---|---|---|
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